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(54) Washing Bleached Fish

(57) Residual bleaching agent is removed from bleached fish without excessive take-up of washing water by contacting with an aqueous solution of alkali metal bicarbonate or carbonate, preferably a solution of sodium or potassium bicarbonate. The weight ratio of fish to liquor normally employed is in the range of 1:2.5 to 1:30 and frequently 1:3 to 1:10. The concentration of the solution normally employed is in the range of 0.05 to 0.15 moles per litre and the temperature of the solution normally falls in the range of 0 to 30°C and frequently at ambient temperature ±5°C. The fish flesh is finally washed with a dilute catalase solution and its pH is thereafter adjusted to within the range of pH 6.0 to 6.5. The process is particularly applicable to H_2O_2 bleaching processes.

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SPECIFICATION
Washing

The present invention relates to the process for the treatment of fish.

In our earlier British patent Specification No. 1,512,843, we have described a process for the whitening of dark fish flesh, including the flesh of naturally dark fish, such as blue whiting and saithe, or the waste material gleaned from filleting of white fish such as cod, often referred to as threshings, employing hydrogen peroxide in an aqueous solution having an initial pH in the range of 10.5 to 11.5. Use of at least more desirable embodiments described in the aforementioned application can result in a product having acceptable appearance, thereby enabling it to be considered for human consumption. Of course, it is necessary to ensure that the product is free from residual hydrogen peroxide, and that in consequence in order to effect positive removal of the hydrogen peroxide, the whitened fish flesh is contacted with preferably catalase. Although catalase is very efficient at destroying hydrogen peroxide, it is comparatively expensive so that the process would become economically more attractive if a method could be devised by which the quantity of catalase to be employed could be reduced. One way of reducing the amount of catalase is to subject the whitened fish flesh to a series of washing steps, each step comprising contacting the flesh with water for a sufficient period of time to enable the hydrogen peroxide to dissolve in the water and thereafter separating the fish flesh from the aqueous solution. Unfortunately, when the fish flesh is water washed, it absorbs up to approximately its own weight of water so that when the flesh is cooked, it still retains the appearance of uncooked fish and is therefore rendered less attractive to the consumer. The problem of absorption of water by the fish flesh occurs whether it has been previously subjected to whitening with hydrogen peroxide or some other bleaching agent such as sodium hypochlorite.

In consequence, it is an object of the present invention to provide a process for the removal of bleaching agent from whitening fish flesh in which the problem of absorption of water by the fish flesh is ameliorated to at least a certain extent.

According to the present invention there is provided a process for the treatment of fish flesh wherein fish flesh which has been whitened employing an active oxygen or an active chlorine bleaching agent is contacted with an aqueous solution of an alkali metal bicarbonate or carbonate, and thereafter separated from the aqueous solution.

In practice, according to the present invention, the whitened fish flesh is normally washed with a dilute aqueous solution of alkali metal bicarbonate or carbonate, and preferably a dilute solution of sodium or potassium bicarbonate or carbonate. The use of sodium bicarbonate solution is especially desirable. In practice also, as the concentration of alkali metal bicarbonate or carbonate increases, so the whitened fish flesh has a decreasing propensity to absorb water from the solution, until a concentration is attained at which the fish flesh absorbs substantially no water. It will be recognised, therefore, that a higher concentration than the minimum required to prevent the whitened fish flesh absorbing water can be employed, if desired, but that the use of additional reagents inevitably increases the cost of the process, both in respect of the washing stage and also in respect of any subsequent stage of adjusting the pH of the fish to slightly acidic, e.g. pH 6.2. Thus, although a concentration of up to that of a saturated solution can be employed, the concentration normally falls in the range of 0.01 to 0.15 moles per litre, and often not more than 0.1 moles per litre. Generally, the concentration is at least 0.025, and frequently at least 0.05 moles per litre of alkali metal bicarbonate or carbonate.

We have found that where the fish flesh is washed at a temperature in excess of 30°C, there is an increasing tendency for the fish to become partially cooked, at least on the surface, the rate and extent increasing as the temperature is raised further above 30°C, so that in order for the fish flesh to remain substantially uncooked, we prefer that the aqueous washing solution has a temperature of not more than 30°C. In practice, the temperature is normally in the range of 0 to 30°C, and is often in the range of 5 to 25°C and frequently at ambient temperature of the fish flesh ± 5°C. The benefit of employing a temperature in the range of 0 to 30°C is particularly noticable when the washing step follows a whitening process step which was also carried out at a temperature of less than 30°C, e.g. ambient ± 5°C, in that in neither step is the fish flesh cooked to any marked extent so that the product retains its naturally uncooked appearance. On the other hand, if the whitening process step was carried out at a temperature in excess of 30°C, e.g. at 50 to 60°C, then the benefit of washing at a temperature of 0 to 30°C is that no further cooking of the fish flesh takes place.

The whitened fish flesh can be washed with the alkali metal bicarbonate or carbonate solution either batch-wise or continuously. Preferably, during the period of contact of the fish flesh with the solution, the mixture is stirred or agitated continuously. The weight ratio of fish flesh to liquor in the in the mixing vessel is normally in the range of from 1:2.5 to 1:30, and preferably from 1:3 to 1:10. However, it will be recognised that by use of more powerful mixing devices, a weight ratio of less than 1:2 could also be employed or alternatively, washing solution could be allowed to trickle through or sucked through a solid mass of fish flesh. Obviously, the longer the period of continuous washing, or the greater the number of batch washes, the greater will be the proportion of residual bleaching agent removed from the fish

flesh. Of course the actual weight ratio of fish flesh to liquor will also effect the bleaching agent peroxide removal rate. When the batch washing technique is employed, preferably at least two washes are employed. Each batch wash is preferably continued until the concentration of bleaching agent in the solution has reached an approximately equilibrium value, and this is normally attained within a period of from 1 to 3 minutes, but if the solution is permitted to remain in contact with the fish flesh for longer than 3 minutes there appear to be substantially no deleterious effects. A contact period of less than 1 minute appears to be wasteful in that, generally, the aqueous solution in that period of time is not able to bleach out as much bleaching agent as it is able to. When continuous washing is employed, the residence time, i.e. the time in which the fish flesh is in contact with the washing solution on average is suitably at least 5 minutes, e.g. 5 to 10 minutes. It will be understood that the washing period, weight ratio of fish flesh to liquor, and washing temperature are substantially independent of the concentration of alkali metal bicarbonate or carbonate in the washing solution, so that any of the aforementioned concentrations may be used in combination with any weight ratio, and any process carried out for any length of time and any temperature as herein described.

Conveniently, the whitened fish flesh can be separated from the washing solution by conventional dewatering presses and/or centrifuges and/or decanters.

In highly preferred embodiments, when the washing process of the present invention follows an active oxygen bleaching process, during the final washing stage, which in practice is often the third or fourth, catalase solution is added. The step is an added precaution to ensure that all the hydrogen peroxide is removed from the fish. The concentration of catalase solution normally falls in the range of from 0.001 to 1% by weight and preferably in the range of 0.005 to 0.1% by weight. The weight ratio of catalase solution to final washing solution is normally in the range of from 1:30 to 1:300, often giving concentration of catalase in final washing solution of 30 to 1000 ppm by weight. It will be recognised that the amount of catalase solution required for this purpose is much less than if the washing with the aqueous washing solution had not been effected. The step of contacting the fish flesh with catalase solution is conducted in this way because its subsequent addition in an aqueous solution which did not contain the desired amount of alkali metal bicarbonate or carbonate would result in the fish flesh again absorbing water, possibly up to its own weight of water, and thereby negating the advantage of employing the aqueous washing solution earlier. It is also desirable to adjust the pH of the whitened fish flesh to mildly acidic, i.e. in the range of pH 6.0 to 6.5. This can be conveniently effected by the addition of an approved acid, such as citric acid, since the washing step with the aqueous alkali metal bicarbonate or carbonate solution will have adjusted the pH of the fish to mildly alkaline, i.e. in the range of pH 8 to pH 10, even if the whitening steps had earlier been conducted under acid conditions. As with the addition of the catalase, the addition of the acid, e.g. citric acid, is also effected in the presence of the alkali metal bicarbonate or carbonate, to ensure that the fish flesh does not absorb water.

The fish flesh which is washed by a process according to the present invention can have been whitened by any known process employing as bleaching agent an active oxygen-containing compound such as hydrogen peroxide or an addition product of it with an alkali metal salt such as sodium percarbonate, or with an active chlorine-containing compound such as sodium hypochlorite, it being understood that the fish flesh remains in solid state throughout the whitening process, and has not been allowed to absorb any or much water. Preferably, the fish flesh has been whitened by a process as described in copending Patent Application No. 20031/75 in which the fish flesh is contacted with an aqueous hydrogen peroxide solution having an initial pH of from 10.5 to 11.5 and preferably from 10.5 to 11.0, at a temperature in the range of 0 up to 30°C, preferably from 5 to 25°C and frequently at ambient ± 5°C, in a weight ratio of fish flesh to bleaching solution of from 1:3 to 1:30, preferably from 1:4 to 1:8, the concentration of hydrogen peroxide being initially from 0.5 to 1% by weight and the bleaching steps effected for a period of from 10 to 30 minutes, often from 10 to 20 minutes. It will be recognised that in such a bleaching process the weight ratio of fish flesh to hydrogen peroxide is often in the range of from 25:1 to 50:1. It now appears preferable for the bleaching solution to be substantially free of a condensed phosphate like sodium tripolyphosphate in order to discourage the uptake of water by the fish flesh. In preferred embodiments of the bleaching process, the pH of the bleaching solution falls to the range of pH 10.2 to 10.5. Also, the whitened fish flesh can have been obtained from threshings or bleached dark fish such as blue whiting, coley or saithe, and is normally in the finely minced state.

Certain embodiments of the present invention will now be described more fully by way of example.

In the examples and comparisons, the whitened fish flesh was obtained by the following method. Minced cod threshings (10 kg) was mixed with a solution of anhydrous sodium carbonate (160 g) in water (40 litres) in a mixing tank and the mixture was agitated for a period of 5 minutes. Hydrogen peroxide (600 ml, 0.75% w/w) was mixed with the fish mince, and the pH of the solution was adjusted to pH 10.5 by the additon of sodium hydroxide. The mixture was agitated for a further 15 minutes and the fish slurry was then transferred to a press to dewater to approximately its original constitution.

Example 1

In this example, the whitened fish mince was slurried with a solution of sodium bicarbonate (30 litres, 0.075 molar concentration), and the slurry agitated for 2 minutes at ambient temperature. The slurry was then dewatered in a press. The procedure of slurrying the mince and then dewatering it was repeated employing the same conditions. The fish mince was then slurried in a further quantity of sodium bicarbonate solution (40 litres, 0.075 molar concentration) and the pH of the solution was adjusted to 7.5 by the addition of citric acid, with continuous stirring. Catalase solution (200 ml, 0.01% w/w) was added and the mixture agitated for 15 minutes, the pH of the mixture was then adjusted to pH 6.2 by the addition of a further amount of citric acid. The slurry was then dewatered to its original composition employing a press. A small sample of the fish slurry was then contacted with titanium IV sulphate, and the absence of a yellowing indicated that all the hydrogen peroxide had been removed. The fish mince product had an appearance resembling that of fresh cod flesh and had a very similar water content. When it was cooked, it did not have the opaque appearance characteristic of uncooked fish flesh.

Example 2

In this example the procedure of example 1 was followed, with the sole exception that the slurrying of the mince with the bicarbonate solution and the dewatering was not repeated. The product of example 2 contained substantially no hydrogen peroxide and the same water content and appearance as the product of example 1.

Comparison 1

In this comparison, the procedure of example 1 was followed except that the washing solutions contained no sodium bicarbonate. The fish mince product at pH 6.2 had a much more translucent appearance and was found to contain substantially greater amount of water than untreated raw cod mince does. Upon heating it retained its translucent appearance.

Comparison 2

In this comparison, the procedure of example 1 was followed with the exception that the catalase solution was added to an aqueous slurry of fish mince free of sodium bicarbonate. As in comparison 1, the product at pH 6.2 had absorbed a considerable amount of water, and had a similar translucent appearance.

Comparison 3

In this comparison, the procedure of example 1 was followed except that the sodium bicarbonate was replaced by an equimolar amount of sodium hydroxide. Once again, the product had absorbed a large quantity of water and had a translucent appearance when its pH was adjusted to at 6.2.

Comparison 4

In this comparison, the whitened fish mince was washed with a solution of sulphuric acid (40 litres, 0.075 molar concentration), agitated for 2 minutes at ambient temperature and then separated from the solution in a press. The procedure of slurrying with a similar amount of fresh sulphuric acid solution and dewatering was repeated. At this stage, the fish mince had an unacceptable stringy appearance which did not look like normal fish flesh.

Claims

1. A process for the treatment of fish flesh wherein fish flesh which has been whitened employing an active oxygen or an active chlorine bleaching agent is contacted with an aqueous solution of an alkali metal bicarbonate or carbonate and thereafter separated from the aqueous solution.

2. A process as claimed in claim 1 wherein the aqueous solution of the alkali metal bicarbonate or carbonate is an aqueous solution of sodium or potassium bicarbonate or carbonate.

3. A process as claimed in claim 1 or 2 wherein the concentration of the alkali metal bicarbonate or carbonate in the aqueous solution is in the range of from 0.01 to 0.15 moles per litre.

4. A process as claimed in claim 3 wherein the concentration of an aqueous solution of the alkali metal bicarbonate or carbonate is in the range of from 0.05 to 0.1 moles per litre.

5. A process as claimed in any preceding claim wherein the fish is contacted with the aqueous solution at a temperature in the range of from 0 to 30°C.

6. A process as claimed in claim 5 wherein the temperature is at ambient temperature $\pm$ 5°C.

7. A process as claimed in claim 5 or 6 wherein the step of contacting with the aqueous solution follows a whitening process step which was carried out at a temperature of less than 30°C.

8. A process as claimed in any preceding claim wherein the weight ratio of fish flesh to aqueous solution is in the range of from 1:2.5 to 1:30.

9. A process as claimed in any preceding claim wherein the weight ratio of fish flesh to aqueous solution in the range of from 1:3 to 1:10.

10. A process as claimed in claims 1 to 9 wherein the process of contacting the fish flesh with the aqueous solution is carried out in batches.

11. A process as claimed in claim 10 wherein the fish flesh in each batch is in contact with the aqueous solution for a period of from 1 to 3 minutes.

12. A process as claimed in claims 1 to 9 wherein the process of contacting the fish flesh with the aqueous solution is carried out continuously.

13. A process as claimed in claim 12 wherein the fish flesh is in contact with the washing solution for a period of at least 5 minutes when continuous washing is employed.

14. A process according to any preceding claim wherein the process is effected in a plurality of stages, each stage comprising the steps of contacting the fish flesh and thereafter separating it from the aqueous solution.

15. A process as claimed in claim 14 wherein the fish flesh in its final stage is contacted with a solution of catalase.

16. A process as claimed in claim 15 wherein the concentration of catalase in solution is from 30 to 1000 ppm by weight.

17. A process as claimed in any preceding claim wherein the pH of washed fish flesh is thereafter adjusted to within the range of pH 6.0 to 6.5.

18. A process for the treatment of fish flesh substantially as described herein with respect to either of examples 1 or 2.

19. Fish flesh whenever treated by a process claimed in any preceding claim.

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